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The emission probability of π electrons at the local emission region containing a single carbon atom in capped C(5,5) single-walled carbon nanotubes is investigated from electronic and geometrical effects. Owing to electronic effects, the sequence of magnitude of emission probability of π electrons from various local emission regions at the tip is in descending order of T4 (the link region between the tip and the body), T2 and T3 (the middle regions), T1 (the top region), while that at the body is close to 0 due to geometrical effects. The fluctuation in the emission probabilities of π electrons implies that the total energy distribution of emitted electrons at the tip and the image luminescence from the tip are not uniform in essence. Different from electronic effects, geometrical effects are only crucial to the field emission property, and have less influence on the emission probability of π electrons for capped carbon nanotubes. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1461432]

Along with the development in fabricating, processing, and manipulation techniques for large-area well-aligned arrays, carbon nanotube bundles have been successfully applied in flat panel displays as unique ultimate field electron emitters.[1]

Both the experiments[2,3] and theoretical studies[4–6] have showed that the tip as well as defects has predominant effects on field emission of carbon nanotube bundles, and the field emission properties of carbon nanotubes are sensitively dependent on the geometrical and electronic structures of the tip and defects. Moreover, we have verified that the electrons located at the tube body in disordered carbon nanotube films can participate in field emission under enough high electric field, as like electrons in amorphous carbon or diamond films because of similar bond characteristics.[7] Although in the prior studies the whole tip or defects are considered as the emission unit, it appears more reasonable to regard the individual local region containing one single carbon atom as the emission unit at the atomic level. In this letter, we attempt to explore the localized characteristics of electronic states of the local emission regions located at the different spatial sites. By examining and analyzing electronic and geometrical effects on the emission probabilities of electrons, we could propose effective ways of improving the field emission properties of carbon nanotubes.

For a capped single-walled carbon nanotube (SWNT), the high-resolution transmission electron microscopy images[8] showed that the unit cell is formed by a carbon atom and three adjacent carbon atoms in the tip and body. In the present study, the individual local emission region containing one carbon atom, shown as shaded region in Fig. 1(a), is considered as the emission unit. A sealed finite-length cylindrical carbon cage consisting of 480 carbon atoms is chosen to represent one capped armchair C(5,5) nanotube, where both ends are closed by the fullerene-like cap (i.e., half C_{60} molecule). According to their bonding characteristics, local emission regions are conveniently classified as five distinct types, and labeled as T1, T2, T3, and T4 (at the tip) and B5 (at the body), as shown in Fig. 1(b). Linear combination of atomic orbitals for molecular orbital (LCAOMO) cluster method using the discrete variational scheme within the framework of local density approximation is employed.[9]

Figure 2 shows the local density of states (LDOS) of local emission regions at the tip and body. We can see that for the local emission regions at the tip, the LDOS peaks at the both sides of the Fermi level, corresponding to the donor and acceptor states, remarkably shift to the Fermi level in comparison with those at the body, due to the presence of conventional topology defects (i.e., pentagons). The LDOS of T4 at the Fermi level is far larger than those of other local emission regions owing to the local bond network (i.e., local electronic states). Consequently, we can suggest that π electrons at the tip are easily emitted in virtue of these yielding

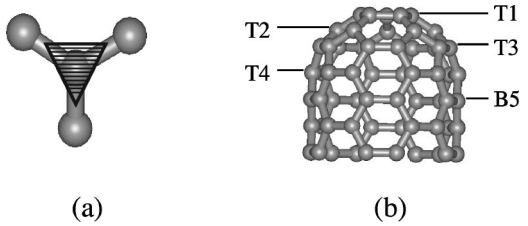

FIG. 1. Geometrical structures of (a) unit cell and (b) single-walled C(5,5) nanotube in our calculations. Symbols T1, T2, T3, T4, and B5 correspond to local emission regions at the tip and body, respectively.

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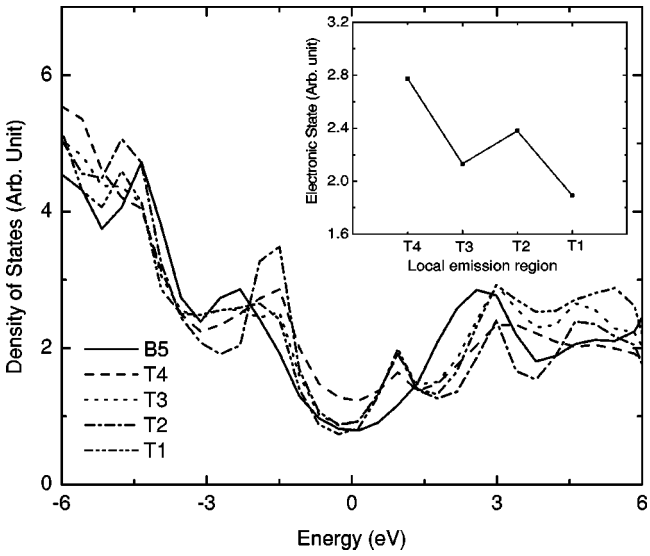

FIG. 2. Local density of states for the local emission regions at the tip and body. Solid, dashed, dotted, dash-dotted and short dashed lines correspond to T1, T2, T3, T4, and B5, respectively. The inset shows the integrating electronic states between the donor states peak and the Fermi level for local emission regions at the tip.

donor or acceptor states under the electric field, which is consistent with other theoretical studies,[4,5] and the emission probabilities of π electrons at the tip are sensitive to the corresponding spatial sites, which is in accordance with the field emission microscopy experiments of multiwalled carbon nanotubes (MWNTs)[10] that revealed a nonhomogeneous spatial charge distribution of the emitting states of a single tube. Figure 2 also shows that the distance between the peak of LDOS (corresponding to the donor states) and the Fermi level is almost identical for all local emission regions except for B5. Thus, herein we integrate the electronic states from the donor states peak to the Fermi level to qualitatively represent the emission probability of π electrons at the local emission region, and the results are shown in the inset of Fig. 2. We could deduce that the emission probabilities of π electrons from the local emission regions at the tip descend in the sequence T4, T2, T3, and T1.

In consideration of the finite number of emitted electrons at the tip and defects, we believe that for the field emission study of carbon nanotubes, it is more reasonable and appropriate to describe the resonant electronic states characteristics in virtue of the energy levels than in virtue of the LDOS mentioned above. Moreover, the knowledge of the discrete energy levels corresponding to local electronic states can be helpful for understanding the correlation between the field emission properties of local emission regions and their spatial positions.

The nature of covalent bond between carbon atoms at the tip[11] and body[12] of carbon nanotubes determines that the valence electrons are only localized in the vicinity of the corresponding carbon atoms. Thus, the localized electronic structure is only related to the interaction behavior of the valence electrons localized at the same site. Within the framework of LCAOMO, one molecular orbital (MO) Ψ_j can be approximated by a linear combination of localized atomic orbitals and delocalized atomic orbitals ϕ_i from various atoms that compose the carbon nanotube. We have

$$\Psi_j = \sum_{i=\text{localized}} C_{ij}\phi_i + \sum_{i=\text{delocalized}} C_{ij}\phi_i, \tag{1}$$

where C_{ij} is the mixing coefficient of atomic orbital, while the square of absolute value for the mixing coefficient, $|C_{ij}|^2$, represents the contribution of atomic orbital ϕ_i to molecular orbital Ψ_j. With the sum of $|C_{ij}|^2$ for localized and delocalized atomic orbitals, we easily make out the characteristics of one molecular orbital and obtain the *localized* molecular orbital that reflects the localized electronic states of one local emission region.

For carbon nanotubes, in the field emission process, the valence electrons are removed from the surface to the vacuum under the electric field and the geometrical structure of one SWNT can be regarded as a huge hollow molecule. The difference in potential energy of one electron between the highest occupied *localized* molecular orbital (HOLMO) and the vacuum level is equal to the corresponding tunneling energy barrier of emitted electrons at the same site. We analyze the localized characteristics of the occupied molecular orbitals below the Fermi level, obtain the HOLMOs for all local emission regions, which are 192 A1 for T4, 189 A1 for T2, 384 E1 for T3, 369 E1 for T1, and 185 A1 for B5. The corresponding tunneling energy barriers are 5.08 eV for T4, 5.48 eV for T2, 6.32 eV for T3, 6.79 eV for T1, and 5.91 eV for B5, respectively. Owing to the similar emission mechanism and process, the tunneling energy barrier for T4 is very close to the work function of SWNTs from the recent experiment.[13] The calculated tunneling energy barriers of the local emission regions indicate that due to electronic effects, π electrons at T4 are first emitted, then those at L2, L3, and finally at L1 and B5, are consistent with the conclusion drawn from the calculated LDOS.

Aiming at the shortage of LDOS in the quantitative description of the field emission characteristics of carbon nanotubes, we systematically analyze the emission probabilities of π electrons at various local emission regions in carbon nanotubes, by virtue of the well known field emission tunneling theory.[14]

Under the electrostatic field, the tunneling probability $D(E)$ for an electron at the energy level E can be represented as

$$D(E) \propto \exp\left(-\frac{4}{3}\frac{\sqrt{2me}}{\hbar}\frac{E_t^{3/2}}{F} \right), \tag{2}$$

where F denotes the electric field and can be given as $F = \beta V$. β is the amplication factor of the local emission region and is mainly related to the geometrical structure,[15] V is the applied voltage, and E_t is the tunneling energy barrier of emitted electrons at the energy level E.

Based on the field emission experiments of carbon nanotubes, the threshold voltage V_{th} is arbitrarily defined as the applied voltage for which a 10^8 A cm^{-2} emission current density J occurs. At this rate, we can obtain the threshold voltages for these local emission regions, which are 29.5 V for T4, 38.3 V for T3, 32.2 V for T2, and 41.7 V for T1 and the calculated emission probabilities of π electrons from the local emission regions at the threshold voltages are shown in Fig. 3. From the figure, we can see that the sequence of the emission probabilities of π electrons at the local emission

regions in carbon nanotubes is, as like the case in the threshold voltages, in descending order of T4, T2, T3, and T1, which is consistent with the conclusions drawn from the corresponding LDOS (as shown in Fig. 2) and tunneling energy barriers and the fluctuation in the emission probabilities of π electrons at these local emission regions is 0.0039, and the corresponding ratio is up to 34.82%. This implies that the total energy distribution of emitted electrons at the tip and the image luminescence from the tip are not uniform in essence. However, to the best of our knowledge, there is no related detailed experimental evidence of this phenomenon to the present.

Our previous study[7] showed that the amplication factor of the body is about 1/125 of that of the tip with the same radius. Therefore, the emission probability of π electrons at the body should be far less than those at the tip due to geometrical effects. Consequently, we can deduce that most electrons are emitted from the tip, and few electrons from the body in the disordered carbon nanotube films at the low applied voltage. By changing the geometrical structure of the local emission region at the body such as introducing defects, the field emission property of the local emission region and the emission probability of π electrons could be drastically enhanced.

As an example that the assumed radius of r_{tip} is equal to 1.0 nm for one SWNT, we further explore electronic and geometrical effects on the emission property and emission probability of emitted electrons in field emission. Many experiments have showed that adjusting the local electronic structure of the emitting region, such as doping active elements that have lower work function (e.g., alkali metal[16,17]) and adsorbing foreign gases (e.g., water[3]), can significantly improve the field emission property of carbon nanotubes. Due to electronic effects, by assuming that the geometrical structure of the SWNT tip does not change, we estimate the threshold voltage and the emission probability of π electrons in the SWNT bundles doped with cesium, which has a work function of only 2.4 eV, and find that the threshold voltage decreases from 86.6 to 36.1 V, which is in accordance with the experimental cases,[16,17] and the emission probability increases by a factor of about 2.7 (from 0.0109 to 0.0294). On the other hand, due to geometrical effects, in the pure SWNT the threshold voltage decreases up to 43.3 V, whereas the emission probability of π electrons does not remain changed with the variation of the radius from 1.0 to 0.5 nm. Evidently, changing the geometrical structure of the emitting region has the same potential on improving the field emission property as adjusting the electronic structure which is employed in the conventional experiments, but has no effect on the emission probability of emitted electrons different from adjusting the electronic structure.

In summary, the emission probability of π electrons at the local emission region in one carbon nanotube is studied. The sequence of the emission probabilities of π electrons is in descending order, T4, T2, T3, T1, B5 owing to electronic effects, while that at the body (i.e., B5) is close to 0 owing to geometrical effects. Meanwhile, the fluctuation in the emission probabilities of π electrons of these local emission regions implies that the total energy distribution of emitted electrons at the tip and the image luminescence from the tip are sensitively dependent on the atomic spatial sites. Like electronic effects, geometrical effects are significant for the field emission property; different from electronic effects, geometrical effects have less influence on the emission probability of π electrons for capped carbon nanotubes. As a result, we suggest that reasonably changing the geometrical structure of the local emission region in carbon nanotubes could be a new and effective means to improve the field emission property.

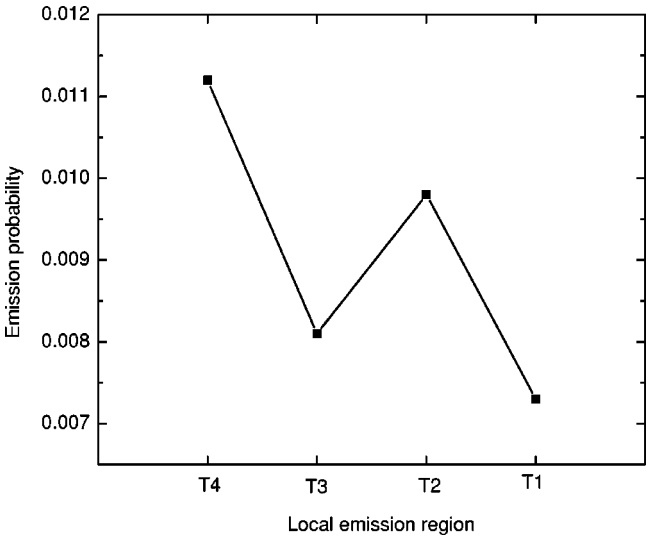

FIG. 3. Emission probabilities of π electrons from the local emission regions of the tip under the threshold voltages.

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[1] Y. Saito, K. Hamaguchi, K. Hata, K. Tohji, A. Kasuya, Y. Nishina, K. Uchida, Y. Tasaka, F. Ikazaki, and M. Yumura, Ultramicroscopy **73**, 1 (1998).
[2] A. G. Rinzler, J. H. Hafner, P. Nikolaev, L. Lou, S. G. Kim, D. Tomanek, P. Nordlander, D. T. Colbert, and R. E. Smalley, Science **269**, 1550 (1995).
[3] K. A. Dean, P. von Allmen, and B. R. Chalamala, J. Vac. Sci. Technol. B **17**, 1959 (1999).
[4] D. L. Carroll, P. Redlich, P. M. Ajayan, J. C. Charlier, X. Blase, A. DeVita, and R. Car, Phys. Rev. Lett. **78**, 2811 (1997).
[5] Ch. Adessi and M. Devel, Phys. Rev. B **62**, 13314 (2000).
[6] G. Zhou, W. H. Duan, and B. L. Gu, Phys. Rev. Lett. **87**, 095504 (2001).
[7] G. Zhou, W. H. Duan, and B. L. Gu, Appl. Phys. Lett. **79**, 836 (2001).
[8] P. M. Ajayan, T. Ichihashi, and S. Iijima, Chem. Phys. Lett. **202**, 384 (1993).
[9] D. E. Ellis and J. P. Perdew, *Density Functional Theory of Molecules, Clusters and Solids* (Kluwer Academic, Boston, 1994).
[10] W. A. de Heer, J.-M. Bonard, K. Fauth, A. Chatelain, L. Forro, and D. Ugarte, Adv. Mater. **9**, 87 (1997).
[11] H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, and R. E. Smalley, Nature (London) **318**, 162 (1985).
[12] G. Zhou, W. H. Duan, and B. L. Gu, Chem. Phys. Lett. **333**, 344 (2001).
[13] D. Lovall, M. Buss, E. Graugnard, R. P. Andres, and R. Reifenberger, Phys. Rev. B **61**, 5683 (2000).
[14] J. W. Gadzuk and E. W. Plummer, Rev. Mod. Phys. **45**, 487 (1973).
[15] W. P. Dyke and W. W. Dolan, Adv. Electron. Electron Phys. **8**, 89 (1956).
[16] S. Suzuki, C. Bower, Y. Watanabe, and O. Zhou, Appl. Phys. Lett. **76**, 4007 (2000).
[17] A. Wadhawan, R. E. Stallcup II, and J. M. Perez, Appl. Phys. Lett. **78**, 108 (2001).